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by

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ISOLATION AND CHARACTERIZATION OF THE ARSORANE $(\text{Me}_3\text{SiCH}_2)_3\text{AsCl}_2$

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ABSTRACT

Reaction of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ with AsCl_3 (1:1 mole ratio) afforded a brown solid and a liquid consisting of $(\text{Me}_3\text{SiCH}_2)_2\text{AsCl}$ and an unidentified substance. Reduction of the liquid with LiAlH_4 gave $(\text{Me}_3\text{SiCH}_2)_2\text{AsH}$ and $(\text{Me}_3\text{SiCH}_2)_3\text{As}$. Reaction of $(\text{Me}_3\text{SiCH}_2)_3\text{As}$ with AsCl_3 produced the crystalline arsorane $(\text{Me}_3\text{SiCH}_2)_3\text{AsCl}_2$ which was characterized by partial elemental analysis (C, H, and Cl), NMR spectroscopy (^1H and $^{13}\text{C}\{^1\text{H}\}$), and mass spectrometry (electron impact).

Key Words: Organoarsenic; arsorane; synthesis; NMR; mass spectrometry; redox

INTRODUCTION

Our research involving the preparation of gallium-arsenic compounds has required a variety of specific new organoarsenic starting materials, including primary and secondary arsines; thus, certain synthetic procedures have had to be developed in our laboratories to meet these needs.⁽¹⁾ Of course, all of the attempts to synthesize desired materials were not productive and, at times, side reactions were significant. For example, reduction of $(\text{Me}_3\text{SiCH}_2)_2\text{AsCl}$ with Zn amalgam in refluxing MeOH resulted in an extremely poor yield of $(\text{Me}_3\text{SiCH}_2)_2\text{AsH}$, but gave

$(\text{Me}_3\text{SiCH}_2)_2\text{AsAs}(\text{CH}_2\text{SiMe}_3)_2$ in a 60% yield.^{1a} On the other hand, reduction of the same chloride with a Zn/Cu amalgam in an $\text{HCl}_{(\text{aq})}/\text{THF}$ solution at room temperature afforded the secondary arsine in 86% yield.^{1b}

In the case of $\text{Me}_3\text{SiCH}_2\text{AsH}_2$, our success in designing a satisfactory overall scheme for its preparation (in 47% yield)^{1c} was not possible without trying other much less rewarding procedures. For example, reaction of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ with As_2O_3 (2:1 mole ratio) in ether, followed by reduction with Zn/Cu amalgam, produced $\text{Me}_3\text{SiCH}_2\text{AsH}_2$ in only 4% yield and $(\text{Me}_3\text{SiCH}_2)_2\text{AsH}$ in 60% yield.² Here we report a scheme which failed to give any of the primary arsine, but rather gave results which prompted a follow-up experiment; viz., reaction of $(\text{Me}_3\text{SiCH}_2)_3\text{As}$ with AsCl_3 , with one product being the new arsorane $(\text{Me}_3\text{SiCH}_2)_3\text{AsCl}_2$.

EXPERIMENTAL

General Information

All manipulations and reactions were carried out either in Schlenk or standard apparatus, I^2R glove bags, or a Vacuum/Atmospheres HE-43 Dri Lab under an inert atmosphere (argon or nitrogen), or on a vacuum line. Deionized water was degassed prior to use. Organic solvents were distilled from sodium benzophenone ketyl, CaH_2 , or P_2O_5 under nitrogen. AsCl_3 and LiAlH_4 were purchased from Alfa Products, Inc., and $\text{Me}_3\text{SiCH}_2\text{Cl}$ from Petrarch Systems, Inc. All commercially available reagents were not further purified. $\text{Me}_3\text{SiCH}_2\text{MgCl}$ and $(\text{Me}_3\text{SiCH}_2)_3\text{As}$ were prepared by the respective literature methods^{3,4}. ^1H NMR spectra were recorded on an IBM NR-80 spectrometer and ^{13}C NMR spectra were obtained on a Joel FX-90Q. All spectra were referenced to TMS using the residual protons or the carbons of the deuterated solvents as the chemical shift reference; for ^1H , $\text{C}_6\text{D}_5\text{H}$ δ 7.15, for $^{13}\text{C}\{^1\text{H}\}$, C_6D_6 δ 128.0. All NMR tubes were flame-sealed under vacuum. The electron impact mass spectrum was recorded on an HP 5988 A mass spectrometer. The melting point



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measurement was made by using a Buchi 510 apparatus and a flame-sealed capillary. Elemental analyses were carried out by E+R Microanalytical Laboratory, Inc., Corona, NY.

Reaction of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ with AsCl_3 and Subsequent Reduction with LiAlH_4

Freshly prepared $\text{Me}_3\text{SiCH}_2\text{MgCl}$ [$\text{Me}_3\text{SiCH}_2\text{Cl}$ (5.55 g, 45.2 mmol) and Mg (1.25 g, 51.4 mmol)] was transferred to a dropping funnel attached to a 3-necked flask containing AsCl_3 (8.2 g, 45.2 mmol) dissolved in an ether/pentane mixture, and equipped with a stir-bar and an argon inlet. The Grignard was added dropwise to the stirred solution at -78° and, on warming, the resultant mixture steadily turned browner. After filtration and washing with pentane, distillation of solvents from the filtrate left a liquid and a brown precipitate. Subsequent filtration with benzene washing, followed by removal of the benzene from the filtrate, afforded a clear yellow liquid and a very small amount of a colorless crystalline solid. ^1H NMR of liquid (C_6D_6): δ 0.08, 1.25 [$(\text{Me}_3\text{SiCH}_2)_2\text{AsCl}$]^{1b}; δ 0.23, 2.64 (X). ^1H NMR of solid (C_6D_6): δ 0.23, 2.64 (X).

Slow addition of LiAlH_4 (1.0 g, 26 mmol) to a THF solution of the yellow liquid resulted in a very exothermic reaction and the formation of a brown mixture, filtration of which yielded a yellow filtrate and solid (7 g). Hydrolysis of the solid (performed in a glove bag) gave an orange-brown slush which was mixed with *conc* HCl and extracted with ether; after drying the extract with MgSO_4 and removal of the solvents and a small quantity of butanol by distillation at atmospheric pressure, there remained $(\text{Me}_3\text{SiCH}_2)_2\text{AsH}$ and $(\text{Me}_3\text{SiCH}_2)_3\text{As}$ (identified from ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the mixture which were comparable to those of authentic samples). *In vacuo* evaporation of volatiles from the yellow filtrate gave a yellow solid [IR (nujol, KBr plates): cm^{-1} 2050 (m, AsH), 1300 (w), 1250 (s), 1050 (s, br), 840 (vs, br), 780 (s), 770 (s), 700 (s), 680 (s)]. After addition of methanol to the solid, all volatiles were removed

under vacuum; only methanol, THF and $(\text{Me}_3\text{SiCH}_2)_2\text{AsH}$ were evident in the ^1H NMR spectrum of the combined evaporates.

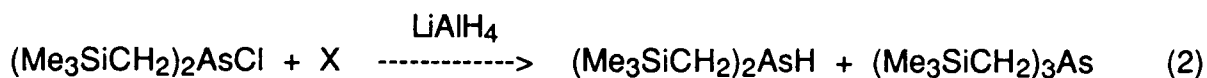
Reaction of $(\text{Me}_3\text{SiCH}_2)_3\text{As}$ with AsCl_3 : Isolation of $(\text{Me}_3\text{SiCH}_2)_3\text{AsCl}_2$

A small quantity of ether and AsCl_3 (0.76 g, 4.2 mmol) were combined with a hexane/benzene solution of $(\text{Me}_3\text{SiCH}_2)_3\text{As}$ (2.0 g, 5.9 mmol) in a reaction tube which was heated to dissolve all of the latter reactant (total volume ca. 10 mL). A brown solid began to precipitate as soon as the AsCl_3 was added; and after 24 h, 0.033 g of brown solid was isolated by filtration. The filtrate was allowed to stand 39 days in a stoppered flask before re-filtration; 0.175 g of brown solid (presumably elemental As) was separated. Volatiles were removed from the filtrate leaving a wet solid [^1H NMR (C_6D_6 , 80 MHz): δ major peaks 0.25 (s, Me_3Si), 2.71 (s, CH_2); δ minor peaks 0.04, 0.12, 0.14 (Me_3Si), 0.66, 0.72, 0.76, 1.94, 2.39 (CH_2)] which was recrystallized from ligroin to yield crystals containing fine brown powder. Dissolution of the latter in C_6H_6 , followed by filtration through a fine frit covered with dry alumina powder, *in vacuo* evaporation of solvent from the filtrate, and two subsequent recrystallizations from ligroin afforded white crystalline $(\text{Me}_3\text{SiCH}_2)_3\text{AsCl}_2$ (0.43 g, 17% yield, mp 112-114.5 °C). Anal. Calcd. (Found) for $\text{C}_{12}\text{H}_{33}\text{Si}_3\text{AsCl}_2$: C 35.37 (35.68), H 8.16 (8.37), Cl 17.40 (17.12). ^1H NMR (C_6D_6 , 80 MHz): δ 0.25 (s, Me_3Si), 2.71 (s, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 22.5 MHz): δ 0.48 (s, Me_3Si), 44.36 (s, CH_2). Mass spectrum (70 eV, scan at 140 °C): selected m/e (abundance) 391 (20%) [$(\text{M} - \text{Me})^+$], 371 (100%) [$(\text{M} - \text{Cl})^+$], 336 (5%) [$(\text{Me}_3\text{SiCH}_2)_3\text{As}^+$], 249 (10%) [$(\text{Me}_3\text{SiCH}_2)_2\text{As}^+$], 145 (20%) [AsCl_2^+], 73 (60%) [Me_3Si^+].

RESULTS AND DISCUSSION

Combining $\text{Me}_3\text{SiCH}_2\text{MgCl}$ with AsCl_3 (1:1 mole ratio) in an ether/pentane mixture at -78 °C, followed by warming to room temperature, afforded a brown solid (presumably

elemental As) and a yellow liquid. Based on its ^1H NMR spectrum, the liquid appeared to consist only of $(\text{Me}_3\text{SiCH}_2)_2\text{AsCl}$ and an unidentified compound (X) (eq. 1); reduction with LiAlH_4 gave $(\text{Me}_3\text{SiCH}_2)_2\text{AsH}$ and $(\text{Me}_3\text{SiCH}_2)_3\text{As}$ (eq. 2).



Others have observed elemental As during reactions between alkyl Grignard reagents and AsCl_3 .^{5,6} Its formation has been explained by the reduction of AsCl_3 by the trialkylarsine;⁶ however, to the best of our knowledge the identity of the oxidation product has never been reported. Considering these observations and our results, it seemed plausible to assume that $\text{Me}_3\text{SiCH}_2\text{MgCl}$ and AsCl_3 had reacted to yield some $(\text{Me}_3\text{SiCH}_2)_3\text{As}$ which then underwent a redox reaction with AsCl_3 to give elemental As and $(\text{Me}_3\text{SiCH}_2)_3\text{AsCl}_2$. On testing this assumption, we indeed found that reaction of $(\text{Me}_3\text{SiCH}_2)_3\text{As}$ with AsCl_3 produced a brown powder and the arsorane as a white crystalline substance (eq. 3); the latter being characterized by



partial elemental analysis (C, H, and Cl), mass spectrometry (electron impact), and NMR spectroscopy (^1H and $^{13}\text{C}\{^1\text{H}\}$). The ^1H NMR spectrum of $(\text{Me}_3\text{SiCH}_2)_3\text{AsCl}_2$ [δ 0.25 (Me_3Si), 2.71 (CH_2)] resembled that of X (eq. 3) (δ 0.23, 2.64).

Finally, it should be noted that a more well known reaction of tertiary arsines with arsenic trihalides is the redistribution reaction which yields a mixture of R_3As , R_2AsX , RAsX_2 , and AsX_3 ; the ratio of products is dependent on the mole ratio of the reactants, the reaction temperature and time, and the R group.^{5,7} Thus, heating Ph_3As with AsCl_3 gives redistribution products almost exclusively and the kinetics of this reaction have been investigated.⁸ On the other hand, although redistributions between $(\text{CH}_2\text{CH})_3\text{As}$ and AsCl_3 or AsBr_3 , and between Et_3As and AsBr_3 have been used as a

synthetic method for the respective primary and secondary arsenic halides, the formation of unidentified black solid indicates that a redox process occurs as well in these particular reactions.⁹

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